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Blue photoluminescence of sponge-like highly porous alumina synthesized in hydrofluoric acid based electrolytes

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Abstract. For the first time nanostructures of anodized aluminum oxide (AAO) were synthesized using hydrofluoric acid based electrolytes under potentiostatic mode with varied oxidation conditions. As-grown oxide layers were amorphous and had sponge-like disordered structure with ramified pores system of 50 to 300 nm diameters. All samples under daylight demonstrated blue emission with power up to 10 μW that was seen by naked eye. It was shown that integral intensity of photoluminescence (PL) emission band in 350 – 650 range increases up to 7 – 60 times depending on synthesis details. Observed PL spectra were approximated by superposition of two components with E_{max} = 2.74 and 2.44 eV, FWHM = 0.63 and 0.53 eV. It was substantiated that studied emission have intrinsic origin and can be attributed to F_2^{2+}- and F_2-centers.

1. Introduction

Porous structures of AAO are widely used as templates for fabrication of ordered periodic arrays of 0D and 1D nanomaterials [1]. Unique physical and chemical properties allow to utilize it as functional medium for forming of composite structures [2], producing of filters [3], thermoconducting coatings [4], active elements of optoelectronics [5] etc.

Numerous studies considering luminescent properties of anodic aluminum oxide synthesized in electrolytes of various type and composition have been conducted up to date [6-22]. The most intensive emission with maximum in 430 - 500 nm range was demonstrated by amorphous as-grown nanostructures anodized in oxalic acid based solutions [6-9]. A major contribution in mechanisms of observed luminescence were made by defects attributed to oxygen vacancies in different charge state [7, 10-18] and/or oxalate-ions impurities [8, 9, 19-22]. Therefore, it is of current interest to search for optimal anodizing modes and electrolytes composition in order to obtain nanostructured oxide layers with high concentration of optically active defects formed due to developed surface with big specific area. The aim of this work was to study photoluminescent characteristics of highly porous AAO structures synthesized using hydrofluoric acid (HF) based electrolytes under varied conditions of electrochemical oxidation.

2. Experimental

A foil of A5 (99.5 %) aluminum with thickness of 500 μm was used as original material. A surface was cleaned preliminarily using ultrasonic bath for 10 min. One-step anodic oxidation was conducted under potentiostatic mode at T_A = 1 °C constant temperature. CV Digma two-electrode electrochemical cell was used with AKIP-1125 power supply and UT-2.6 thermocontroller. A solution of hydrofluoric acid in ethylene glycol was used as electrolyte. Two groups of samples using different conditions were

obtained. A constant C_{HF} = 0.9 M electrolyte concentration and varied voltage in U_A = 75 - 400 V range was applied for the first one. A constant U_A = 150 V and altered concentration in C_{HF} = 0.9 – 10 M range was used for the second group. All samples were cleaned after the process. Anodized region was a circle with 2.5 cm diameter. For more details regarding synthesis process see [23].

Surface images of AAO were obtained by using Carl Zeiss SIGMA VP scanning electron microscope with InLens detector in high vacuum. Phase composition was analyzed by means of PANalytical X'Pert Pro diffractometer with Cu K_α (0.1541 nm) line.

Emission spectra of photoluminescence within 350 - 650 nm range were registered at room temperature in phosphorescence mode using Perkin Elmer LS 55 spectrometer. All samples were excited with photons in 277 ± 10 nm band [23]. Slit widths of monochromators in excitation and registration channels were adjusted to 10 and 5 nm, respectively. Speed of spectra scanning was 120 nm/min. To evaluate photometric characteristics Vega OPHIR meter with PD 300 standard photodiode based detectors was used.

3. Results

Synthesized alumina was in amorphous state according to XRD analysis within 2θ = 10 - 90 °range. Figure 1 shows SEM images of grown structures surfaces. It is seen that anodized layer is characterized by sponge-like structure with ramified system of pores with various diameters of 50 to 300 nm. Oxide layer of sample with C_{HF} = 2.5 M and U_A = 150 V was ≈ 20 μm thick.

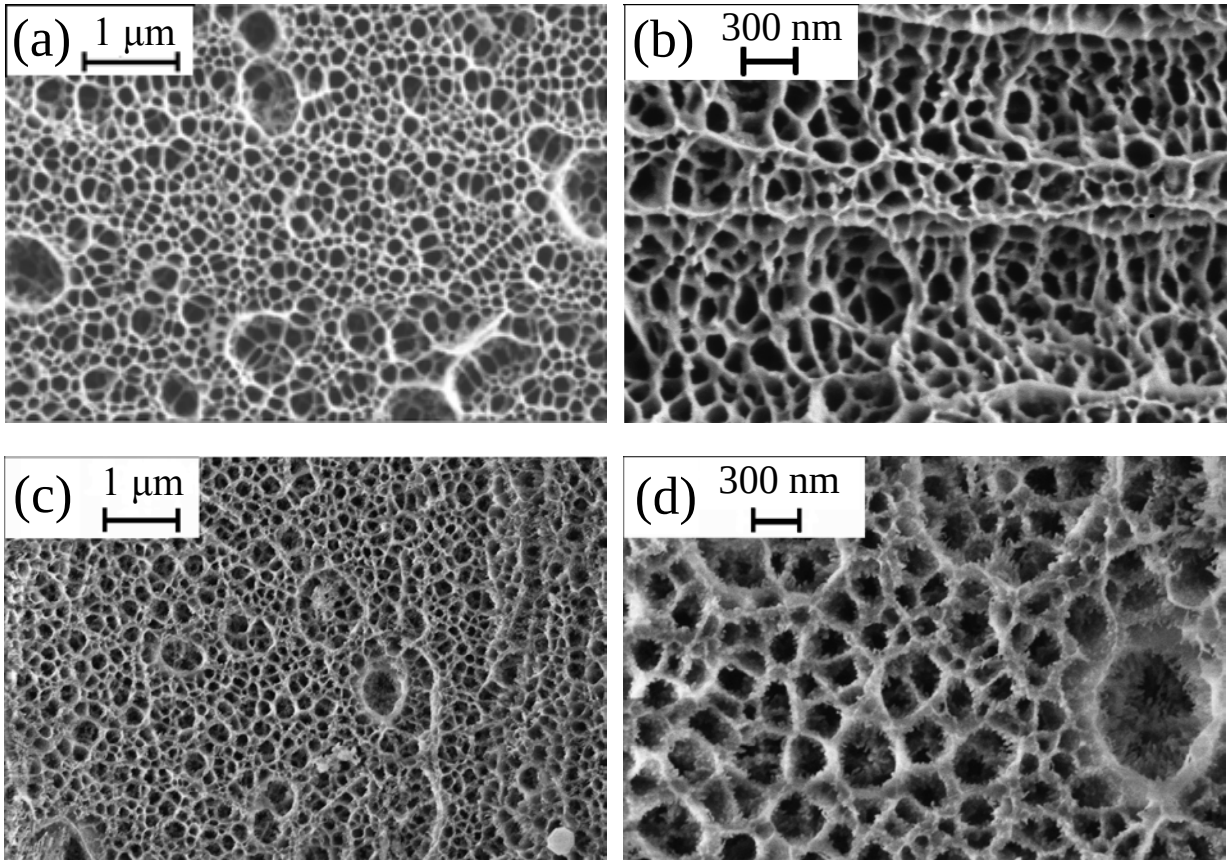

Figure 1. SEM surface images of AAO: 0.9 M, 150 V (a, b) and 5.1 M, 150 V (c, d).

It was found that under daylight highly porous oxide has blue emission with power up to 10 μW that was seen by naked eye. Figure 2 and 3 shows measured spectra for varied U_A and C_{HF} anodizing

parameters. The integral intensity of PL emission in studied range increases up to 60 times due to voltage changes from 75 to 400 V, see inset in Figure 2. Relative integral intensity grows by 7 times within concentration change range, see inset in Figure 3. Samples with the most intensive emission were the ones synthesized in electrolytes with C_{HF} = 5.1 and 6.2 M. Concentration and anodizing voltage increase can lead to growth of oxide layer thickness, specific effective surface area and, therefore, cause a rise for luminescence response of samples. Further studies with use of independent methods are necessary to reliably assess indicated correlation.

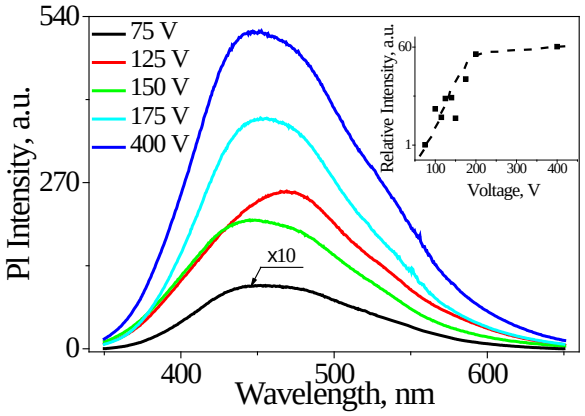

Figure 2. PL emission spectra for different U_A. Inset: relative changes of integral PL intensity.

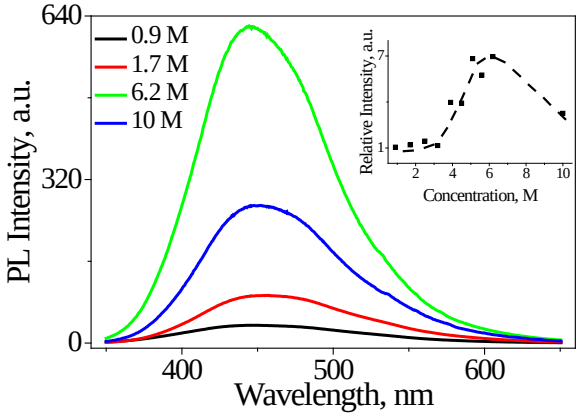

Figure 3. PL emission spectra for different C_{HF}. Inset: relative changes of integral PL intensity.

4. Discussion

Normalized experimental PL spectra of samples are shown in Figure 4. It can be concluded that registered peak is non-elementary since λ_{max} maximum position changes in 440 to 480 range and differences in shape are present for various synthesis modes. It is in agreement with known data regarding values of λ_{max} for AAO synthesized in oxalic acid – 420 nm [16], 430 nm [12], 450 nm [11], 480 nm [15] etc. PL spectra were approximated by superposition of two Gaussian bands, see examples in Figure 5. Precision of quantitative description of all experimental data for resulting curves was $R^2 > 0.999$ (coefficient of determination). Calculated values of E_{max} energy and FWHM halfwidth for each Gaussian component after averaging are listed in Table 1. It is to be noted that obtained values are in satisfactory agreement with each other in shown ± 0.05 eV scatter.

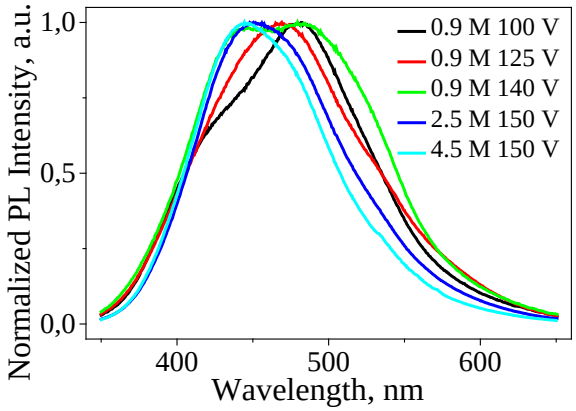

Figure 4. Normalized PL spectra of AAO.

It is known that luminescence centers of AAO synthesized in $(COOH)_2$ are complexes based on oxygen vacancies and/or oxalate-ions impurities formed during oxidation process [7-22]. Electrolyte composition in current work excluded presence of oxalate-ions. As far as data about spectral

characteristics of vacancy based centers with different charge states in single crystalline α-Al_2O_3 is concerned it can be supposed that observed emission has intrinsic origin and can be attributed to F_2^{2+}-centers (2.66 eV [24-26]) for G1 peak and to F_2-centers (2.4, 2.46 eV [24-26], 2.38 eV [27]) for G2 one. Also, various relative concentrations of optically active centers can cause scatter of spectral and kinetic characteristics of photo- and thermally stimulated processes in aluminum oxide [28]. Thus, observed geometrical parameters variations of studied nanostructures spectra could be due to different concentration ratios of corresponding defects because of anodizing modes alteration.

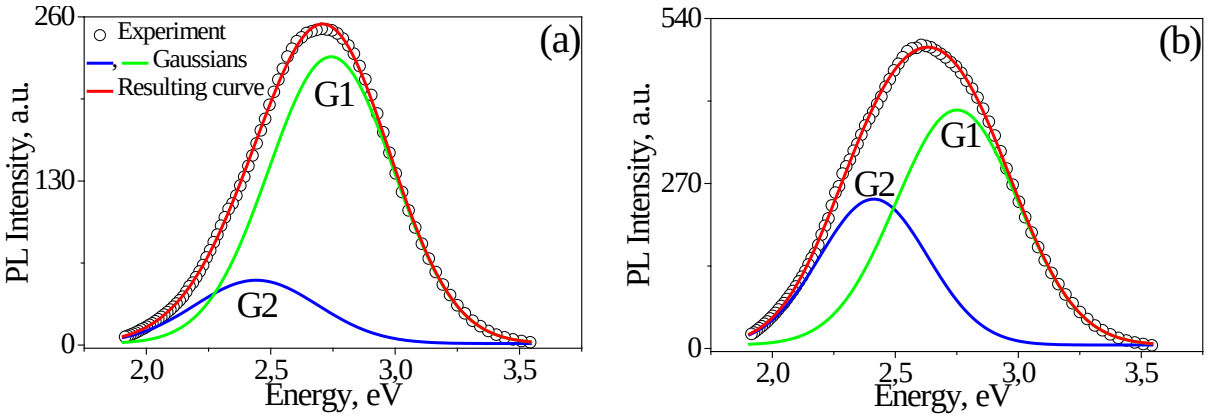

Figure 5. Deconvolution of PL spectra: 5.6 M HF, 150 V (a) and 0.9 M HF, 200 V (b).

Table 1. Calculated parameters of spectral components.

	E_{max} (±0.05 eV)	FWHM (±0.05 eV)
G1	2.74	0.63
G2	2.44	0.53

5. Conclusions

For the first time structures of sponge-like highly porous AAO were fabricated by anodic oxidation under potentiostatic modeusing hydrofluoric acid based electrolytes. Voltage was varied within U_A = 75 - 400 V range and concentration were altered in C_{HF} = 0.9 - 10 M diapason during nanostructures synthesis. It was shown that obtained oxide layers are characterized by unordered sponge-like morphology with ramified system of poreswith 50 to 300 nm diameters. Under daylight grown oxide structures had blue emission that was seen by naked eye. It was found that integral intensity of PL emission in 350 - 650 nm range grows by 7 - 60 times due to variation of anodizing parameters. Experimental spectra were approximated by superposition of two Gaussian bands with high degree of precision. Calculated parameters of spectral components E_{max} = 2.74 and 2.44 eV, FWHM = 0.63 and 0.53 eV were analyzed in comparison with independent literature data. It was concluded that studied PL has intrinsic origin and can be attributed to F_2^{2+}- and F_2-centers. Concentration ratios of discussed vacancy based defects are varied depending on anodizing conditions and cause observed changes of maximum position and luminescence band shape in synthesized samples.

Acknowledgements

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